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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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To cite this Article Langlois, Bernard R. , Billard, Thierry , Guerin, Sophie , Large, Sylvie and Roidot-Perol, Nathalie(1999) 'Electrophilic Trifluoromethylation of Vinyl Sulfides', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 153: 1, 323 – 324

To link to this Article: DOI: 10.1080/10426509908546452

URL: <http://dx.doi.org/10.1080/10426509908546452>

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Electrophilic Trifluoromethylation of Vinyl Sulfides

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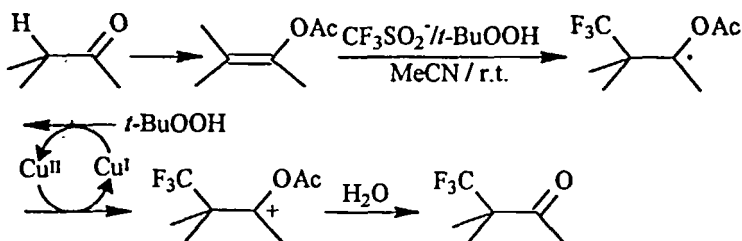
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Thioketals of α -(trifluoromethyl)ketones were prepared from $\text{CF}_3\text{SO}_2\text{Na}$, *t*-BuOOH, methanol, catalytic Cu(II) and vinyl sulfides.

Keywords: vinyl sulfides; trifluoromethylation; sodium triflinat

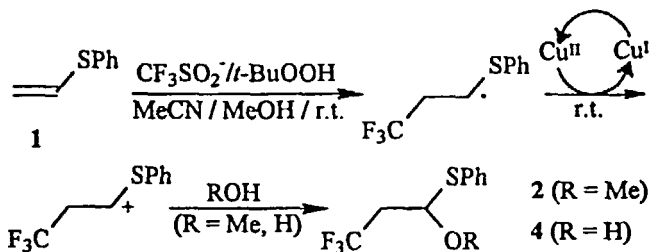
INTRODUCTION

Single-electron oxidation of sodium triflate ($\text{CF}_3\text{SO}_2\text{Na}$) by *t*-butyl hydroperoxide delivers the electrophilic trifluoromethyl radical which can be trapped by disulfides^[1], aromatics^[2] or enol esters^[3]. In the two latter cases, provided that Cu(II) is added as catalyst, the reaction results in the formal substitution of a proton by an equivalent of a $^+\text{CF}_3$ cation. From ketones, the following mechanism has been proposed^[3].



RESULTS AND DISCUSSION

The same reaction has been applied to phenyl vinyl sulfide **1**. However, the resulting trifluoromethylated cation, strongly stabilized by the sulfur atom, cannot evolve through deprotonation to provide a trifluoromethylated vinyl sulfide. In order to prevent polymerization, it must be trapped by a nucleophile: methanol, used as co-solvent with acetonitrile, is an adequate one. Thus, α -(trifluoromethyl)thioacetal **2**, which constitutes a protected form of α -(trifluoromethyl)acetaldehyde **3**, was formed (crude yield: 54 %, isolated yield: 41 %). Water, brought by *t*-BuOOH, was also a minor trapping agent which delivered α -(trifluoromethyl)hemithioacetal **4** (crude yield: 20 %). During chromatography, **4** was deprotected to volatile **3**. Nevertheless, to obtain the best results, **1** must not be in contact with unsolvated Cu(II) since, in this case, it was oxidized to acetylene and diphenyl disulfide to a large extent. When Cu(II) was solvated by methanol prior addition of **1**, this oxidation occurred to a very small extent, as shown from the amount of PhSCF₃ resulting from PhSSPh and $\cdot\text{CF}_3$ (yield: 7 %): **2** and **4** were obtained in fair yields.



Because of the stabilization of anions in α -position to a sulfur atom, it can be imagined that **2** could be deprotonated then alkylated, constituting, in this respect, a valuable equivalent of the $\text{CF}_3\text{CH}_2\text{C(O)}^-$ anion.

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